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FREE RADICALS PRODUCED IN TATB BY UV IRRADIATION.(U)
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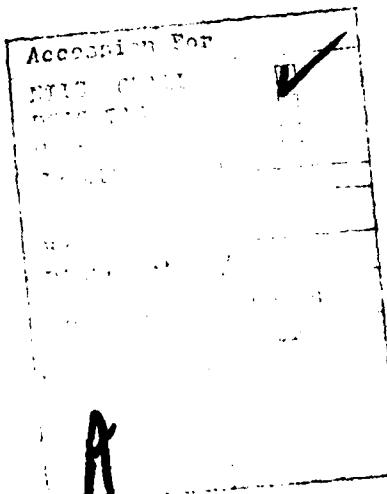
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20. KEY WORDS (Continue on reverse side if necessary and identify by block number) Electron Spin Resonance; TATB; free radicals	21. ABSTRACT (Continue on reverse side if necessary and identify by block number) TATB exposed to ultraviolet irradiation gradually darkens from yellow to black. Using electron spin resonance spectroscopy, we found that free radical formation accompanies the discoloration, and that the UV-generated radicals are stable to temperatures of ca. 220°C. Treatment of irradiated TATB with dimethylsulfoxide yielded a soluble free radical, identified from its hyperfine structure as a hydrogen atom adduct of TATB.	

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Free Radicals Produced in TNTB
by U-V Irradiation

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ULTRAVIOLET IRRADIATION OF TATB:

Generally, energetic materials exhibit increasing shock sensitivity with increasing performance.¹ Since this trend suggests that usable performance is limited by safety considerations, there has been a great deal of interest in so-called "wooden explosives" which are unusually insensitive for their energy content. TATB (1,3,5-triamino, 2,4,6-trinitrobenzene) is exceptional in this respect.

When TATB is exposed to broadband ultraviolet radiation, the material gradually darkens from yellow to black. Using electron resonance (ESR), we have found that free radical formation accompanies the discoloration, and that these UV-generated radicals are remarkably stable.

Figure 1 shows the ESR spectrum characteristic of UV irradiated powder samples of TATB, an asymmetric line having a peak-to-trough width of 7 C. Most of the irradiations were carried out in air room temperature on Pantex samples² containing residual NH₄Cl from synthesis. However, no differences were found either when these samples were leached in boiling water prior to irradiation, or when chlorine-free samples synthesized from TNT³ were used. The same spectrum also appeared when irradiation was performed in vacuo at liquid nitrogen temperature. ESR saturation effects were observed at power levels of about 20 mw., so spectra were generally taken at power levels of only a few milliwatts. All solid samples examined were powders. While TATB is crystalline in form⁴, the material has low solubility, so single crystals sufficiently large for ESR studies are presently unavailable.

We carried out *in situ* irradiation experiments to examine radical production rate. The free radical level rose rapidly at first, but the rate of formation gradually decreased on further irradiation. This behavior is apparently due to UV opacity of the sample, radical formation being more rapid at exposed surfaces and slower in the sample interior where the radical flux is lower.

For this reason, we tumbled the samples during irradiation to expose as much new surface area as possible; Fig. 2 illustrates the arrangement. The source, not shown in the figure, was a 600 watt mercury-xenon arc lamp focused in a beam about 2 cm in diameter. TATB powder was placed in the 5 mm. quartz NMR tube, which in turn was kept in a water jacket to minimize heating. The end of the NMR tube was rotated by a rotor using a short piece of rubber tubing as a flexible coupling. Radical yields of about one radical per hundred molecules were obtained in this way.

Since the radicals were quite stable under ambient conditions, variable temperature studies were performed to determine thermal stability. Experimental results are shown in Fig. 3. Spectra were taken from room temperature up to 300 C° in 20 C° increments, dwelling 10 min. at each temperature. This allowed adequate time to obtain a spectrum after about 3 min. of equilibration, while ensuring reproducibility in the presence of kinetic behavior. Figure 3 shows the spin density as a function of temperature. This was obtained by double integration of the ESR spectrum, and then compensating for temperature dependence of polarization per spin using the Curie law. No change in free radical level occurs until about 220 C°, where the

number of spins begins to decrease. This is accompanied by a lineshape change to a slightly broader spectrum (Fig. 4a) with a peak-to-trough linewidth of 13 G. At 300 C°, this spectrum decays exponentially with a time constant of 55 min.

Gaseous doping experiments were carried out on irradiated samples using bromine and ammonia. Broad, nearly symmetric lines resulted, shown in Figs. 4b and 4c; peak-to-trough linewidths were 14 and 10 G. for bromine and ammonia respectively. The line centers fell within about one gauss of each other, too close for significance to be attached to the different *q* values.

Two pieces of evidence exist which point to steric hindrance as the factor which stabilizes the free radical. Drs. A.N. Garboway and H.A. Rosing (NRL) have run solid state proton nuclear magnetic resonance experiments which indicate that little or no NH₂ motion is present below about 200 C°, above this in the vicinity of 222 C° the free radicals observed by ESR begin to decay. Secondly, in the course of solution studies discussed below, we found that the solid state free radical spectrum changed after the sample was wet with dimethyl sulfoxide as shown in Fig. 4d. The effect is irreversible in that the lineshape remained altered after subsequent drying. For these two cases, at least, a relaxation of lattice rigidity by thermal or solvent mechanisms is accompanied by a change in the free radical signal.

SOLUTION DERIVATIVES OF THE SOLID RADICAL

When UV irradiated TATB is treated with dimethyl sulfoxide (DMSO),

the solution has a slightly darker color compared to the pale yellow solution obtained from the non-irradiated powder. If the solution prepared from irradiated powder is examined by ESR, one obtains a multi-line spectrum from a dissolved free radical species.

The spectrum is observed whether the solution is prepared in the presence or absence of air, although oxygen was generally excluded to avoid possible line broadening. The radicals have a lifetime on the order of a hour when exposed to air, but last for several days when the solvent is degassed.

The free radicals remaining in the parent solid are considerably more stable than those in the liquid phase, even though a lineshape change of the solid radical occurs when the irradiated powder is moistened with DMSO, as shown in Fig. 4d. In fact, we found that after the liquid radical decayed completely, the solution could be renewed by warming it with the parent TATB.

Glassware shown in Fig. 5 was constructed by Dr. A.D. Britt (NRL). Arms A and B were used for the initial degassing procedure. Irradiated TATB powder (typically 50 mg.) was placed in arm A. A small amount (about 1 cc.) of DMSO was placed in arm B, which could be immersed in liquid nitrogen for degassing. After several freeze-pump-thaw cycles, the neck of the apparatus was sealed off under vacuum. The DMSO was then mixed with the powder in arm A, and a small amount of the solution was poured into the capillary tube of arm C. The function of this thin tube was to restrict the amount of DMSO which is lossy at the microwave frequencies used in ESR.

Figure 6 shows spectra of the liquid radical, one taken at room

temperature, the other just below the boiling point of DMSO (about 55°C under vacuum). The greater resolution and symmetry at the higher temperature can be attributed to more efficient rotational averaging of anisotropies. The spectrum is symmetric, indicative of a single species, but even at the higher temperature, resolution is incomplete, since the lines are generally broader than the 30 mg. limit imposed by the 100 kHz field modulation frequency. The measured g value was 2.0044, characteristic of a nitro-aromatic species.⁵ Tetracene dissolved in concentrated sulfuric acid was used as a reference.⁶ A preliminary identification of this free radical has been made by Dr. A.D. Britt (NBS); the chemical structure and splitting constants are indicated in Fig. 7a. This radical differs from the species originally present in the irradiated solid. Evaporation of the DMSO from the solution and examination of the powder residue yields the spectrum shown in Fig. 7b, which is clearly different from that shown in Fig. 1.

REFERENCES

1. Private communication, L.C. Smith, WM-2, Los Alamos Sci. Lab.
2. Manufactured at DUE Partex facility, supplied courtesy E.D. Loughran, WM-2, Los Alamos Sci. Lab.
3. Supplied courtesy John Kolb, Lawrence Livermore Laboratory. For a comparison between so-called normal and chlorine-free TMB, see H.R. Flores, J.R. Humphrey and J.R. Kolb, Lawrence Livermore Laboratory Report UCRL - 52562.
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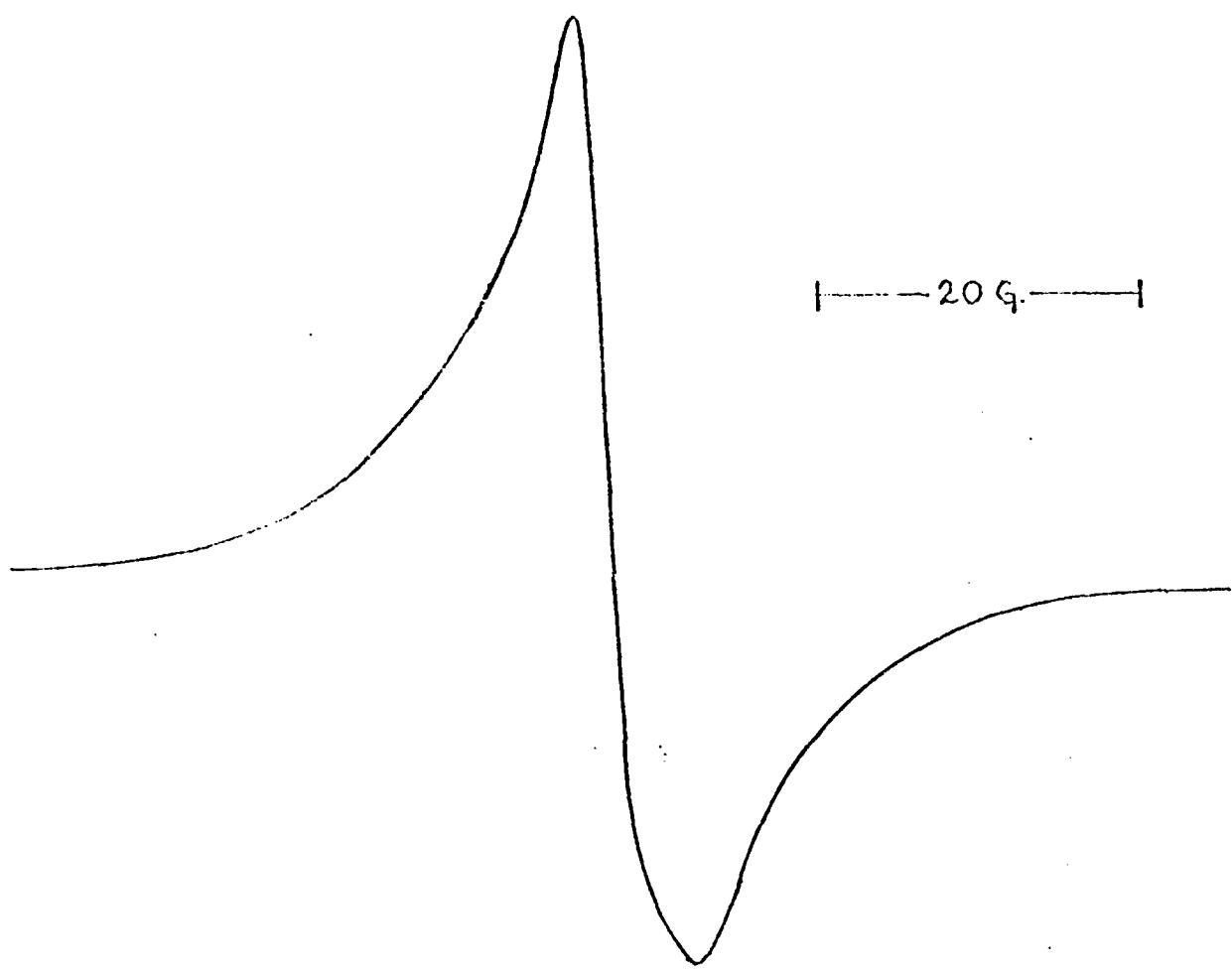


Figure 1. ESR spectrum obtained from ultraviolet irradiated TATB powder.

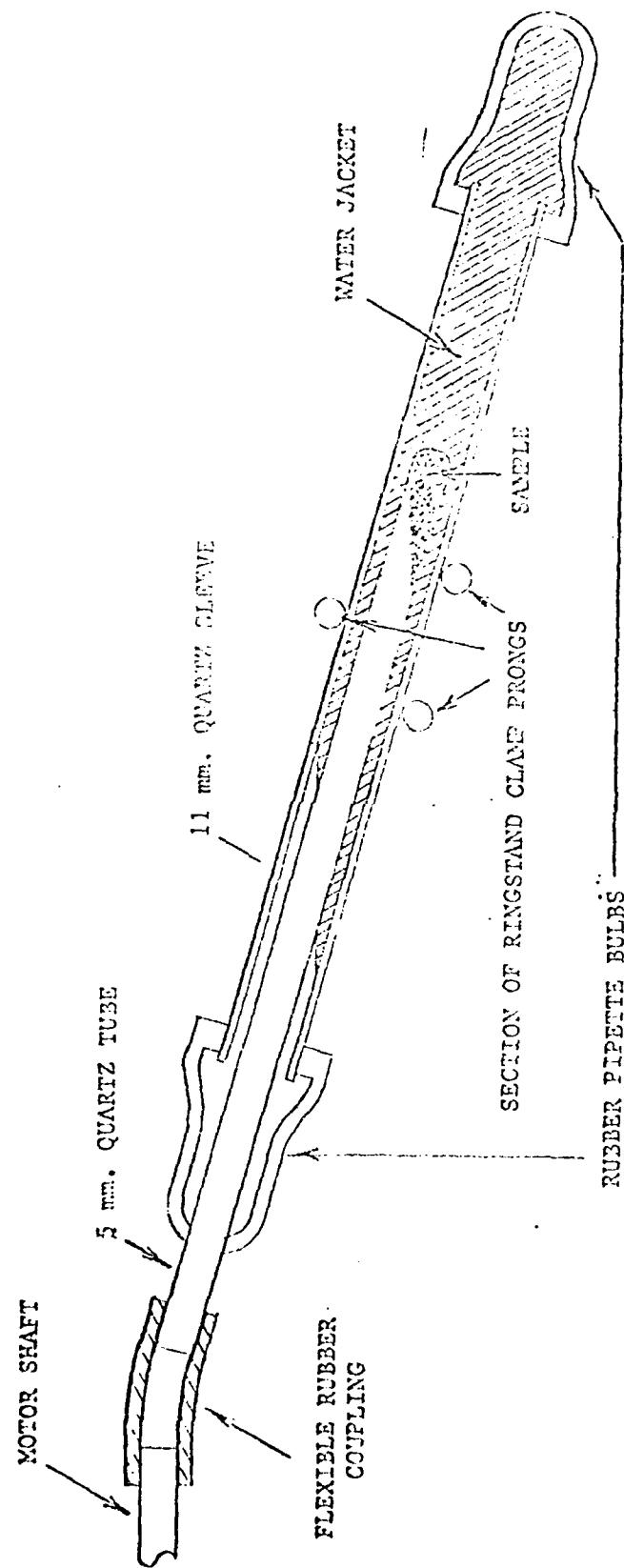


Figure 2. Apparatus used for ultraviolet irradiation of TATB powder. The sample is aligned in the beam (not indicated) by adjusting the ringstand clamp and motor positions. The tube is nearly horizontal so that all the powder is exposed to radiation by tumbling. The water jacket prevents excessive sample heating.

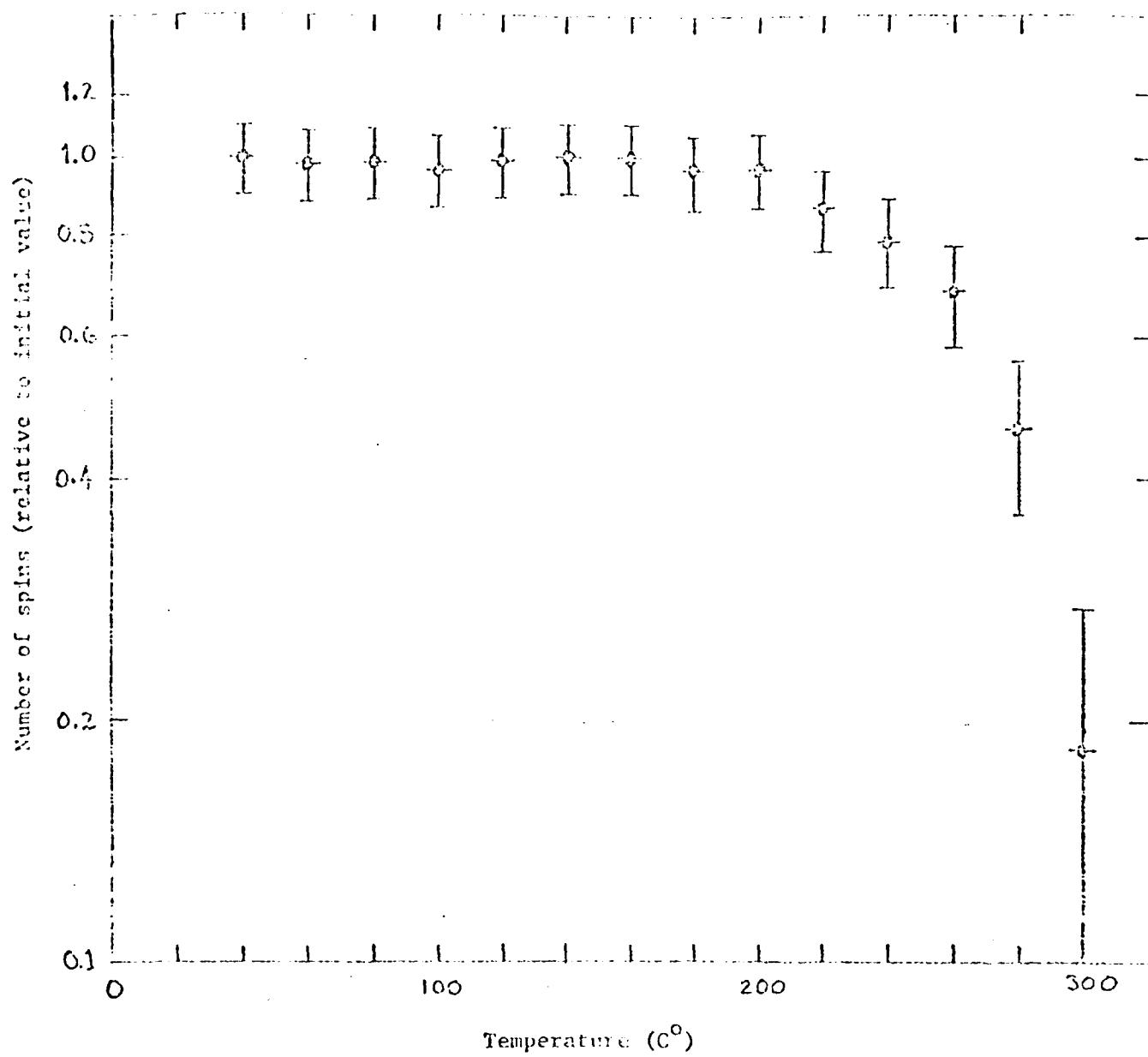
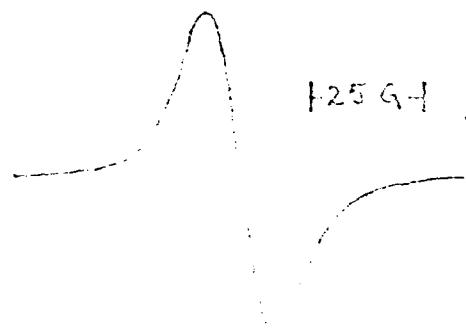
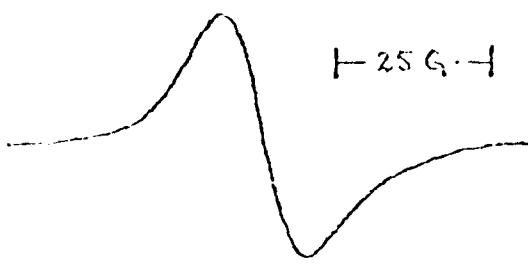


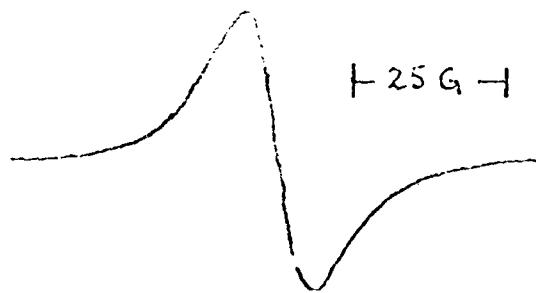
Figure 3. Thermal decay of free radicals produced by ultraviolet irradiation of the solid. The number of spins is obtained by double integration of the absorption-derivative ESR spectrum present at each temperature; Curie law behavior was assumed by weighting each point by its temperature in K°. The sample temperature was increased by 20 C° every ten minutes.



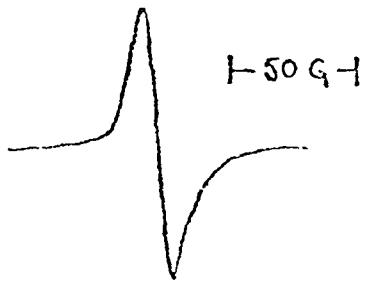
(a) Heating to 150°C in air



(b) Exposure to Br_2



(c) Exposure to NH_3



(d) Moistening with DMSO

Figure 4. Spectra obtained after treatment of UV irradiated TATB.

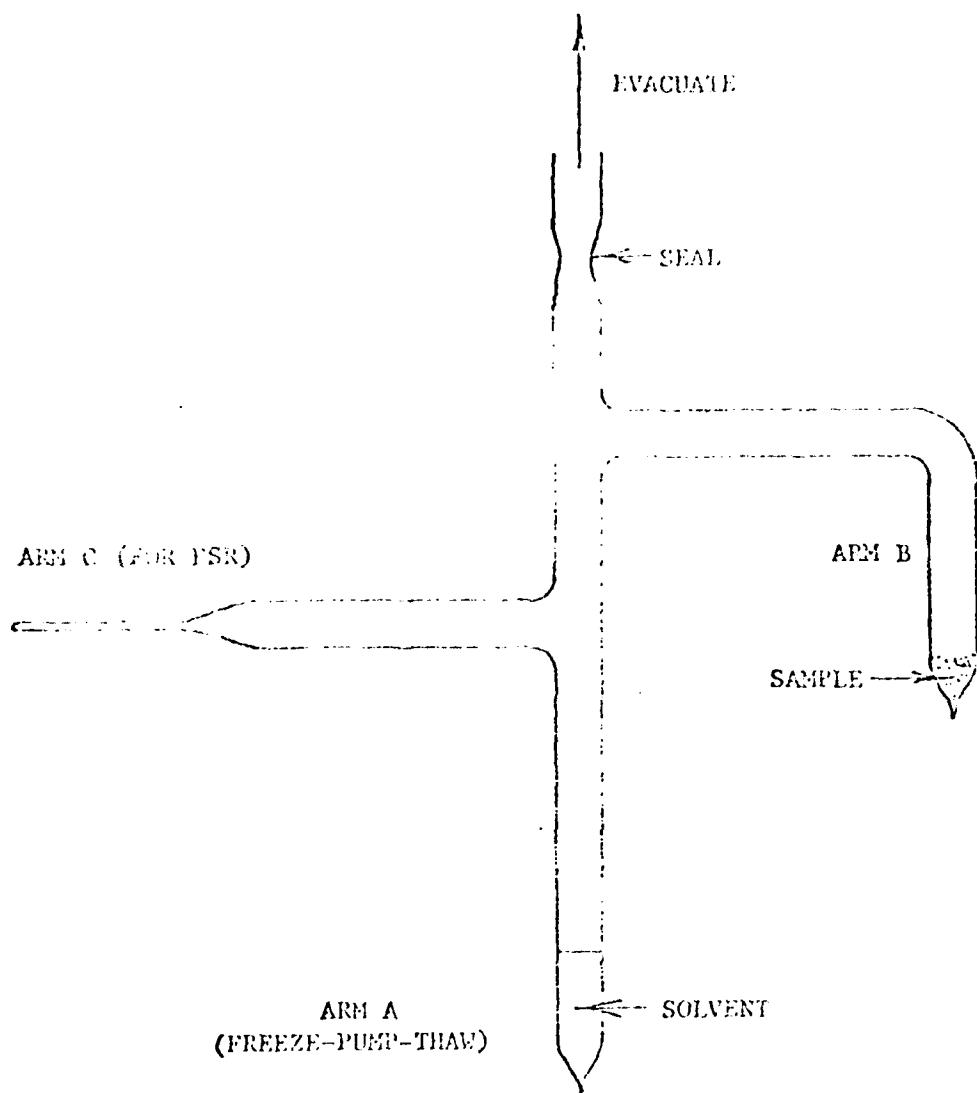


Figure 5. Glassware used for preparation of liquid state free radicals from irradiated TATB. Arms A and B are used during solvent degassing and mixing, while arm C is used for observation. The narrow capillary limits the amount of polar solvent to avoid excessive microwave loss when arm C is placed in the cavity.

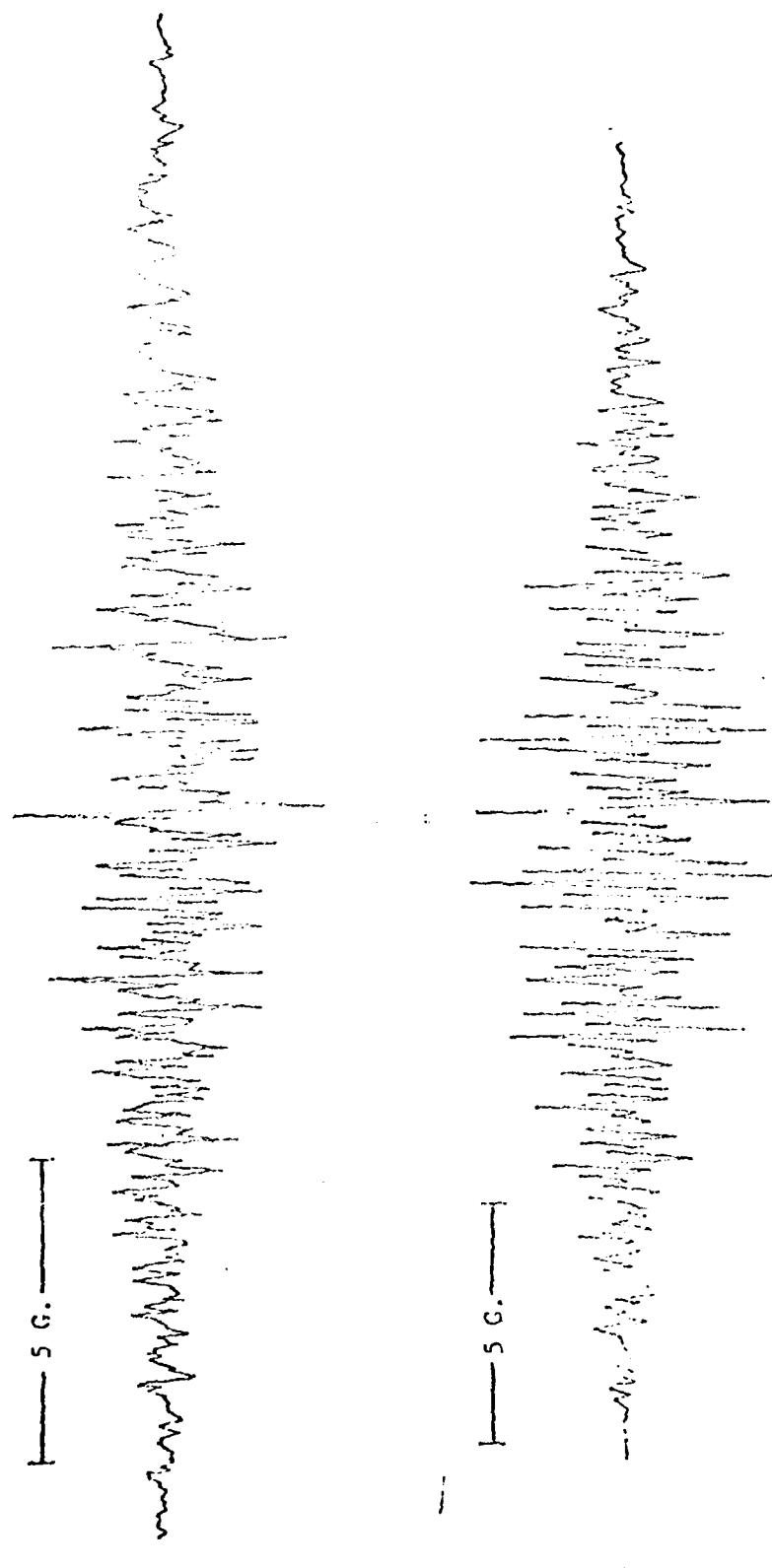


Figure 6. ESR solution spectra obtained by dissolving ultraviolet irradiated TATB in DMSO. The upper spectrum is obtained at room temperature. Moderate warming to 55°C alters the spectrum to the form shown in the lower trace. The effect is reversible.

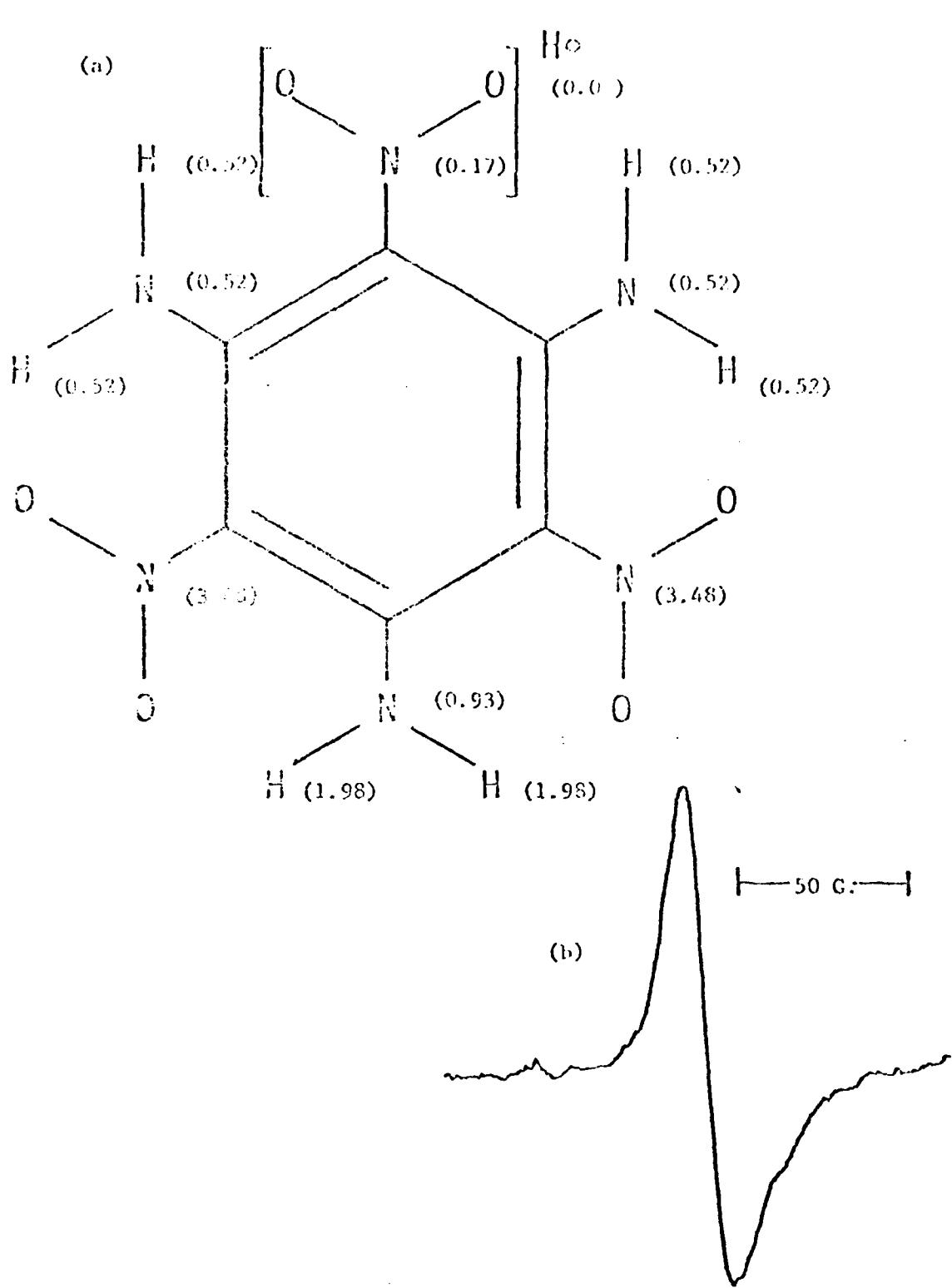


Figure 7. (a) Preliminary assignment of radical obtained by dissolving ultraviolet irradiated TATB in DMSO. The numbers show the assigned nuclear hyperfine couplings in gauss.
 (b) ESR spectrum of residue left behind after DMSO is evaporated from solution.

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